

Original Paper

Determination of trace perchlorate in river water by ion chromatography with online matrix removal and sample concentration

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Abstract

This paper proposes a simple ion chromatographic approach to determine trace amounts of perchlorate in river water samples. Determination of the trace perchlorate by ion chromatography typically faces two challenges: interference by matrix ions such as chloride, nitrate, and sulfate in the samples and insufficient detection sensitivity. In the present study, online pretreatment of the samples with an OnGuard II Ba/Ag/H disposable sample pretreatment cartridge prevented the sulfate peak tailing from overlapping with the perchlorate peak on the chromatogram. In addition, the matrix removal enabled as large as 10 mL of sample to be loaded into a high exchange capacity anion concentrator, significantly improving perchlorate's detection sensitivity. The proposed approach achieved a detection limit ($S/N = 3$) of $0.046 \mu\text{g L}^{-1}$ without using a costly mass spectrometer and successfully determined sub $\mu\text{g L}^{-1}$ levels of perchlorate in river water.

Keywords Perchlorate, ion chromatography, river water, solid phase extraction, preconcentration.

Statements and Declarations

The authors have no competing interests to declare relevant to this article's content.

Introduction

Perchlorate (ClO_4^-) is one of the environmental pollutants, and its influence on the human body has attracted much attention. Its main applications include rocket and missile fuels, gunpowder, and fireworks [1, 2]. It was reported that Chile's nitrate fertilizers contained relatively large amounts of ClO_4^- [1]. Hypochlorite solutions contain trace amounts of ClO_4^- that form during and after manufacture [2]. Naturally occurring ClO_4^- produced photochemically in the atmosphere falls to the ground as wet depositions [3]. ClO_4^- is characterized by its lack of polarity, which makes it stable and resistant to decomposition, and by its extremely high solubility in water [4]. The latter characteristic results in the quick uptake of food and drinking water. Thus, ClO_4^- has recently been detected in foods such as milk, eggs, lettuce, and spinach [5-7]. Humans need to ingest iodine to synthesize thyroid hormones, which are essential for developing nervous tissue [8]. The thyroid hormones regulate numerous biochemical reactions, including protein synthesis and enzyme activities, and play critical roles in determining metabolic activities. They are also necessary for the normal development of the fetus and infant's skeletal and central nervous systems [9]. ClO_4^- competitively inhibits iodine absorption by the thyroid gland's sodium iodide symporter (NIS) and may decrease thyroid hormone production [10]. It has been noted that this may cause hypothyroidism and impaired brain development in fetuses and infants [11].

In 2005, the National Academy of Sciences (NAS) recommended a Reference Dose (RfD) of $0.7 \mu\text{g kg}^{-1} \text{day}^{-1}$ for ClO_4^- [1]. The US Environmental Protection Agency (US EPA) adopted the RfD of ClO_4^- in the NAS and proposed a provisional Health Advisory Level (HAL) of $15 \mu\text{g L}^{-1}$ for drinking water [12]. In Japan, ClO_4^- of $0.08 - 340 \mu\text{g L}^{-1}$ was found in the Tone River in Tokyo in 2007 [13]. These high ClO_4^- concentrations can be attributed to wastewater from ClO_4^- compound manufacturing plants. In 2009, ClO_4^- was designated as an item for consideration in water quality standards based on the Water Supply Law by the Ministry of Health, Labour, and Welfare. A target value of $25 \mu\text{g L}^{-1}$ in water supply was set in April 2011 [14].

Determination methods for ClO_4^- include X-ray fluorometry [15], spectrophotometry [16], surface-enhanced Raman scattering (SERS) [17], and ion chromatography (IC) [13, 18, 19]. IC is widely used to determine ClO_4^- due to its superior separation from coexisting ion species and detection sensitivity. EPA Methods 314.0 [20] and 314.1 [21] require using IC fitted with an electrical conductivity detector to determine ClO_4^- in drinking water and wastewater. However, two problems have arisen when using IC to determine the ClO_4^- in river water. First, the matrix, such as chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) in river water, exist at the mg L^{-1} levels [22], and these matrix peaks interfere with the trace ClO_4^- peak. The ClO_4^- peak may overlap the tailing portion of the SO_4^{2-} peak, which is contained at exceptionally high concentrations [23, 24]. Second, the IC sensitivity is insufficient for detecting the low ClO_4^- concentration in river water at the $\mu\text{g L}^{-1}$ levels [18, 25]. Combining IC with costly mass spectrometry (MS) or MS/MS improves the detection sensitivity of ClO_4^- [13]. Preconcentration of samples using a concentrator column is also helpful in enhancing the IC sensitivity for ClO_4^- [26, 27].

The present paper demonstrates the elimination of matrix interferences and the improvement of ClO_4^- detection sensitivity without MS. River water samples pass online through a disposable sample pretreatment cartridge and an anion concentrator column and are analyzed by IC. The matrix removal rate and sample loading volume were studied, and the optimized ClO_4^- determination system was evaluated in the field application.

Experimental

Reagents and samples

Deionized water was produced using Sartorius Arium ®611DI ($>18 \text{ M}\Omega \text{ cm}$). All reagents used in the present study were of analytical grade, purchased from Kanto Chemical Co., Inc. The standard ClO_4^- solutions were prepared from sodium perchlorate or potassium perchlorate. The Cl^- , NO_3^- , and SO_4^{2-} in the pseudo-river water samples were prepared from sodium salts. Sodium hydroxide (NaOH) was used as

the eluent of IC. River water samples were collected from the Shikoku region, Japan, and filtered with a 0.45 μm pore size membrane filter (Minisart RC25, Sartorius Stedim Biotech). The samples were stored in polypropylene bottles at 4°C until analysis.

Instruments

A schematic diagram of the perchlorate determination system is shown in Fig. 1. A 10 mL-capacity V6 syringe pump (SP, Kloehn Co. Ltd.), equipped with a 6-way injection valve (IV, Kloehn Co. Ltd.) was used to deliver the sample/standard solution and water. A personal computer controlled the sample aspiration/dispensation volume, flow rate, and flow channel. An OnGuard II Ba/Ag/H disposable sample pretreatment cartridge (PTC, 2.5 cc, Dionex Corp.) consisted of three layers, i.e., a styrene-based sulfonic acid resin in the barium-form, silver-form, and hydrogen-form. The barium and silver resins removed SO_4^{2-} and Cl^- by precipitation, respectively. The hydrogen resin trapped soluble silver and other cations in the sample matrix. A male Luer lock fitting (VPRM106, ISIS Co., Ltd.) and a female Luer to 10-32 female (P-629, IDEX Health & Science KK) were used as the adapters for the PTC.

An ICS-1000 ion chromatograph (all chromatographic hardware/software: Dionex Corp.) equipped with an IonPac AS20 4 \times 250 mm separation column (SC) and an ASRS ULTRA II 4 mm self-regenerating suppressor (Sup) was used for the perchlorate determination. An IonPac UTAC-LP2 4 \times 35 mm anion concentrator column (ACC) was a high exchange capacity column (25 $\mu\text{eq}/\text{column}$) suitable for extensive sample loading. The column heater temperature was set at 35°C. The eluent of 10 mol L^{-1} NaOH (EL) was pumped by a high-pressure liquid pump (LP) at a flow rate of 1.5 mL min^{-1} . The output signals of the conductivity detector (CD) and system control were acquired under software control (Chromleon Ver. 6.8).

A series of ClO_4^- determination procedures are as follows. IV was switched to an injection mode, and then the SP aspirated 10 mL of water at 15 mL min^{-1} and wasted it for the syringe cleaning. SP aspirated 10 mL of water at 15 mL min^{-1} and dispensed it to PTC at 2.0 mL min^{-1} for PTC conditioning

and cleaning the flow channels. SP aspirated 6.0 mL of the sample/standard at 15 mL min⁻¹ and dispensed it to PTC at 2.0 mL min⁻¹ for the co-washing of the syringe and flow channels. IV was switched to a loading mode, and SP aspirated a definite volume of sample/standard at 15 mL min⁻¹ and dispensed it to ACC at 2.0 mL min⁻¹. IV was switched to the injection mode, and IC detected the perchlorate eluted from ACC.

Results and Discussion

Matrix removal with sample pretreatment cartridge

The matrix removal rates with PTC were evaluated using pseudo-river water samples containing 1.0 mg L⁻¹ ClO₄⁻, 2.0 mg L⁻¹ Cl⁻, 1.0 mg L⁻¹ NO₃⁻, and 5.0 mg L⁻¹ SO₄²⁻. Note that the matrix concentrations used were selected by considering the median matrix concentrations (1.9 mg L⁻¹ Cl⁻, 1.0 mg L⁻¹ NO₃⁻, 6.2 mg L⁻¹ SO₄²⁻) of 11 real-river water samples from the Shikoku region, Japan. One hundred microliters of the pseudo-river water sample passed through PTC were injected into IC. Figure 2 shows the removal rates of matrix anions and the recovery rate of ClO₄⁻. These rates were calculated from the ratio of the peak height of respective ions with/without PTC. Passing the pseudo-river water sample through PTC removed 100.0 ± 0.01% (*n* = 3) of the Cl⁻ in the sample (Fig. 2a), but very little of the NO₃⁻ (3.4 ± 0.31%, *n* = 3, Fig. 2b) and SO₄²⁻ (-0.11 ± 0.13%, *n* = 3, Fig. 2c). The calcium ions are effective in eluting the barium ions from the resin in the first layer of PTC and precipitating them with SO₄²⁻ [28]. Therefore, to improve the removal rate of SO₄²⁻, 0.50 mol L⁻¹ calcium chloride (CaCl₂) was added to the pseudo sample so that the volume ratio of CaCl₂ solution to sample was 1 : 99. For the samples to which 0.50 mol L⁻¹ CaCl₂ was added, the peak height of respective ions for calculating the removal and recovery rates, *H*_{corr}, was corrected as in Eq. 1.

$$H_{\text{corr}} = H_{\text{meas}} \times \frac{100}{99} \quad 1)$$

where H_{meas} is the peak height of respective ions measured by IC. As shown in Fig. 2c, adding CaCl_2 improved the SO_4^{2-} removal rate to $91.1 \pm 0.7\%$ ($n = 3$). On the other hand, quantitative recoveries of the target ion, ClO_4^- , were obtained with/without the addition of CaCl_2 (Fig. 2d). Unless otherwise stated, the PTC pretreatment was conducted by adding 0.50 mol L^{-1} CaCl_2 to the sample in the following experiments.

The PTCs used in the present study were disposable cartridges. The maximum sample volume that a single PTC could efficiently remove the matrix ions was investigated using pseudo-river water samples. Two hundred milliliters of the pseudo-river water sample were continuously pretreated in a single PTC, of which $100 \mu\text{L}$ at any sample treatment volume was injected into IC. Figure 3 shows the effect of sample treatment volume on the matrix removal. The peak heights of Cl^- and SO_4^{2-} increased gradually with an increase in the sample treatment volume. The Cl^- peak height increased sharply when the sample treatment volume exceeded 170 mL, probably due to the CaCl_2 added to the sample. Depending on the matrix concentration in the sample, a single PTC effectively removes the matrix ions from a hundred or more milliliters of a river water sample.

Perchlorate enrichment with anion concentrator column

The ClO_4^- enrichment capacity with ACC was evaluated using pseudo-river water samples containing $1.0 \mu\text{g L}^{-1}$ ClO_4^- , 2.0 mg L^{-1} Cl^- , 1.0 mg L^{-1} NO_3^- , and 5.0 mg L^{-1} SO_4^{2-} . Note that the ClO_4^- concentration used here was 1000 times lower than that used in the previous section. Figure 4 shows the ClO_4^- peak height as a function of sample volume loaded into ACC. For the PTC pretreatment samples, the ClO_4^- peak height increased linearly up to a sample volume of 10 mL ($r^2 = 0.9900$), while at the sample volumes of 15 mL and 20 mL, the peak heights were lower than predicted values from extrapolation of the regression line. On the other hand, without PTC pretreatment, the ClO_4^- peak heights were lower than those with PTC pretreatment, and there was no linear relationship with the sample volume. These results might be due to the matrix ions retained in the upstream portion of ACC and ClO_4^- diffusing downstream. The matrix

removal with PTC allowed for quantitative ClO_4^- enrichment. The 10 mL of sample loading on ACC was selected in the subsequent experiments.

Validation of analytical procedures

For 10 mL loading of 0, 0.050, 0.10, 0.20, 0.50, 1.0, 1.5, and 2.0 $\mu\text{g L}^{-1}$ ClO_4^- into ACC, the response of the conductivity detector could be expressed as follows.

$$H_{\text{wPTC}} = (0.0406 \pm 0.0013)C + (0.0013 \pm 0.0013), \quad r^2 = 0.9938 \quad 2)$$

$$H_{\text{woPTC}} = (0.0420 \pm 0.0009)C + (0.0008 \pm 0.0008), \quad r^2 = 0.9975 \quad 3)$$

where H_{wPTC} and H_{woPTC} are, respectively, the peak height in $\mu\text{S cm}^{-1}$ with and without PTC pretreatment, and C is the ClO_4^- concentration in $\mu\text{g L}^{-1}$. The slope of the calibration curve with PTC (Eq. 2) agreed with that without PTC (Eq. 3), the slope ratio (with/without PTC) being 0.97. This result indicates that the PTC pretreatment had little effect on the ClO_4^- peak height. Therefore, there is an option to skip the PTC pretreatment for the ClO_4^- calibration curve. In the calibration curve for the sample with the PTC pretreatment, the limit of detection, LOD ($S/N = 3$), and limit of quantitation, LOQ ($S/N = 10$), were calculated to be 0.046 $\mu\text{g L}^{-1}$ and 0.153 $\mu\text{g L}^{-1}$, respectively. The relative standard deviation of repeated measurements for 1.0 $\mu\text{g L}^{-1}$ ClO_4^- in the pseudo-river water sample was 1.74% ($n = 3$). Table 1 summarizes the LOD and LOQ of the ClO_4^- detection method using IC and MS. The detection sensitivity of the present study was inferior to the expensive IC-MS/MS technique [13] but meanwhile, superior to the published preconcentration-IC methods [18, 23] and comparable to the two-dimensional IC approach [30]. In addition, our detection method uses the PTC for pretreatment, simplifying the sample pretreatment process and allowing online pretreatment and detection, resulting in low cost and labor savings.

Application to river water samples

The proposed method was applied to determine ClO_4^- in river water samples. Figure 5 shows the chromatograms of the river water sample with and without PTC pretreatment. Note that the significant peaks that appeared before 5 min are attributed to matrix ions, and the retention time of ClO_4^- was around 10 min. The PTC pretreatment removed a large amount of matrix and allowed the detection of ClO_4^- peak. Eleven samples collected from rivers in the Shikoku region were analyzed using the proposed method, and three were above the LOQ. Spike and recovery tests were carried out by spiking $1.0 \mu\text{g L}^{-1}$ ClO_4^- to the ClO_4^- detected river water samples. As shown in Table 2, sub $\mu\text{g L}^{-1}$ levels of ClO_4^- were successfully detected, and acceptable recoveries were obtained.

In summary, we have demonstrated a determination of trace perchlorate in river water by ion chromatography with online matrix removal and sample concentration. The matrix removal with the sample pretreatment cartridge reduced the interference of matrix peaks on the chromatogram. It increased the optimal amount of sample to be loaded into the anion concentrator column. Without mass spectrometric technique, our approach has successfully detected sub $\mu\text{g L}^{-1}$ levels of ClO_4^- in river water samples.

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Tables

Table 1 Comparison of LOD ($\mu\text{g L}^{-1}$) and LOQ ($\mu\text{g L}^{-1}$) for IC based ClO_4^- detection methods

Method	Sample	LOD	LOQ	Ref.
IC-MS/MS	Groundwater	-	0.05	[13]
HPLC-ICP-MS/MS	Ground, tap, and river water	0.3	-	[29]
Thermal sample concentration IC	River water	0.5	2	[18]
Preconcentration/preelution IC	Groundwater	0.77	-	[23]
Two-dimensional IC	Standard solution	0.055*	-	[28]
Matrix removal/sample concentration IC	River water	0.046	0.153	This study

* Lowest concentration minimum reporting level.

Table 2 Application to river water in the Shikoku region, Japan, $n = 2$ for spike and recovery tests

River sample	$\text{ClO}_4^- /$ $\mu\text{g L}^{-1}$	ClO_4^- , spiked / $\mu\text{g L}^{-1}$ *	Recovery, %	pH	$\text{Cl}^- /$ mg L^{-1}	$\text{NO}_3^- /$ mg L^{-1}	$\text{SO}_4^{2-} /$ mg L^{-1}
Ryuouzan	0.249	Not applicable	Not applicable	8.00	4.06	9.42	13.0
Akuse Valley	0.464	1.41 ± 0.01	94.9 ± 1.0	6.64	2.58	1.10	10.3
Matsuda River	0.368	1.47 ± 0.03	110.1 ± 3.3	6.83	3.56	0.785	2.92

* ClO_4^- concentration found in $1.0 \mu\text{g L}^{-1}$ ClO_4^- spiked river water sample.

Figure Captions

Figure 1 Schematic of the perchlorate determination system.

PTC, pretreatment cartridge; SP, syringe pump; EL, eluent; LP, liquid pump; IV, injection valve; ACC, anion concentrator column; SC, separation column; Sup, suppressor; CD, conductivity detector.

Figure 2 Removal rates of a) Cl^- , b) NO_3^- , and c) SO_4^{2-} and recovery rate of d) ClO_4^- with PTC pretreatment of a pseudo-river water sample, $n = 3$.

W PTC, with PTC pretreatment; CaCl_2 w PTC, 0.50 mol L^{-1} CaCl_2 added to the sample followed by PTC pretreatment.

Figure 3 Peak heights of matrix ions and ClO_4^- ranged a) $\geq 100 \mu\text{S cm}^{-1}$ and b) $\leq 4 \mu\text{S cm}^{-1}$ as a function of sample treatment volume with PTC, $n = 3$.

Figure 4 Relationship between ClO_4^- peak height and sample volume loaded on ACC, $n = 3$.

Figure 5 Typical chromatogram of river water sample with and without PTC pretreatment. The inset shows a magnified view around the ClO_4^- peak. The dotted line in the inset is the manually drawn baseline. The ClO_4^- concentration was calculated to be $0.464 \mu\text{g L}^{-1}$ using the peak height less sensitive to baseline variation.

Fig. 1

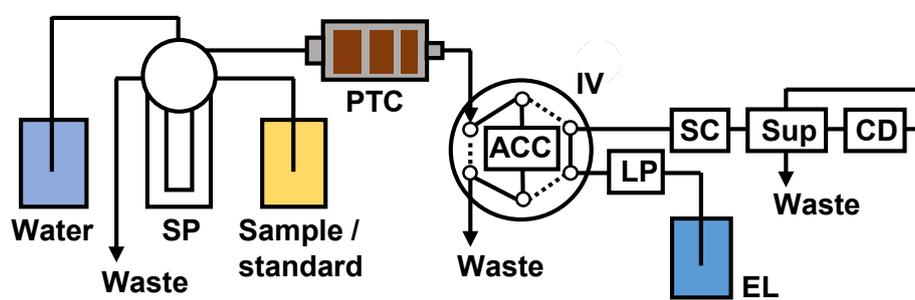


Fig. 2

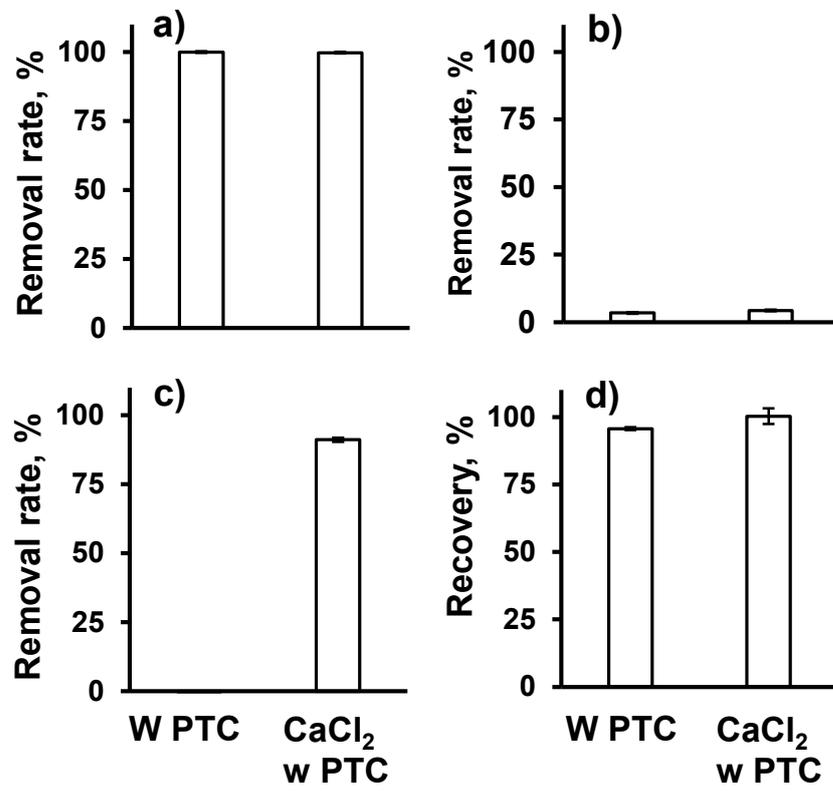


Fig. 3

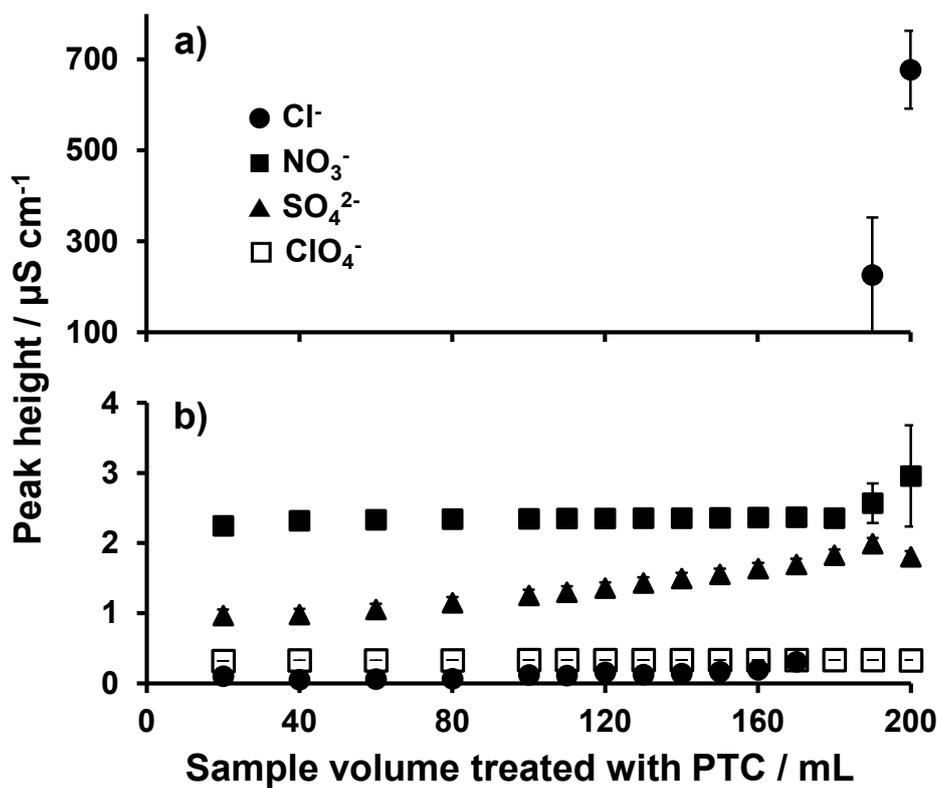


Fig. 4

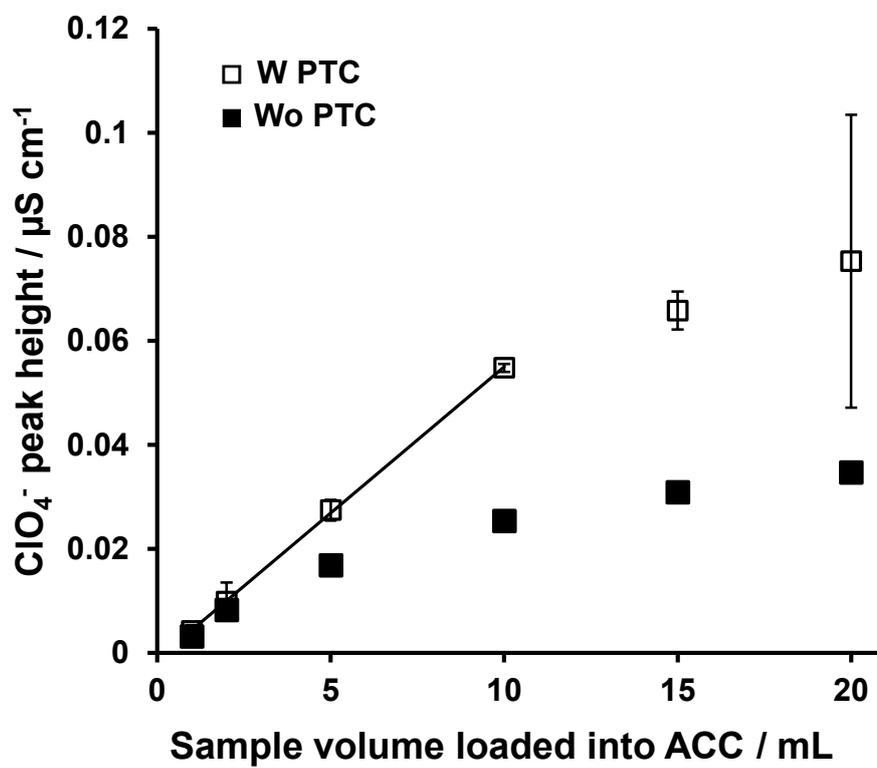


Fig. 5

